which contains a large number of serine, threonine, and glycine residues,[12] does not randomly degrade under the conditions used; moreover, no evidence has been found for the liberation of N-terminal residues other than those mentioned. The possibility of the existence of alkali-labile ester bonds involving serine and threonine hydroxyl groups is ruled out by the fact that succinyl aldolase subunits yield new rather than no N-terminal residues after incubation in alkali. In fact, prior blocking of all free amino groups by succinylation provides a unique method for the detection of newly formed N-terminal amino acids resulting from moderate chemical action.

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Electron Spin Resonance Spectra of *cis*- and *trans*-3,4,5-Trimethoxyphenylglyoxal Semidione Radical Anions

Sir:

Recently the preparation of a number of semidione radical anions containing a single aryl substituent has been reported.[1] In contrast to the case of the aliphatic compounds,[2] the esr spectra of monoaryl semidiones did not show evidence of the presence of *cis* and *trans* isomers. This fact was attributed to the complexity of the spectra which makes the detection of lines of low intensity difficult.

We were stimulated to further investigations on similar molecules, and we chose 3,4,5-trimethoxyphenylglyoxal which was expected to yield a particularly simple spectrum.

The semidione radical may supposedly be prepared in two ways: by the method used by Fraenkel and coworkers,[3] which has been suggested to produce a semidione radical anion when one electrolyzes a solution of benzaldehyde in dimethylformamide (DMF),[1,4] and by the method described by Russell, *et al.*[2]

In one series of experiments we electrolyzed a DMF solution of 3,4,5-trimethoxybenzaldehyde, containing tetraethylammonium perchlorate as supporting electrolyte, with the experimental arrangement already reported.[5] The esr spectrum was recorded as soon as the electrolysis was stopped. In another series of experiments, the 3,4,5-trimethoxy-ω-bromoacetophenone was treated with potassium *t*-butoxide in a dimethyl sulfoxide (DMSO) solution and the esr spectrum of the solution recorded immediately after mixing.

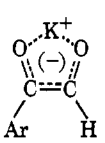
Spectra were recorded with a Varian 4501 X band spectrometer equipped with 100-kc/sec field modulation. Field calibrations were performed with a Harvey–Wells precision gaussmeter whose frequency was measured with a Hewlett–Packard frequency counter.

The esr signals consisted of the same number of lines with approximately the same frequency pattern in both experiments and decayed in about 1 hr to give other more complicated spectra which were not analyzed. In the DMF solution experiments, the signal was analyzed as the superposition of two six-line spectra with an intensity ratio of 1:3 and having their centers 180 mgauss apart. Each of the six-line spectra is composed of two equal 1:2:1 triplets.

In the DMSO experiments the relative intensity of the two spectra is very much dependent on the cation (K^+) concentration; if the latter is high enough only one six-line spectrum is observed and the species to which it refers is the one with the larger single proton coupling. The two species are labeled A and B in Table I, where the values of the coupling constants are summarized together with those obtained for the phenylglyoxal semidione radical anion[1,3] (C). It is to be noted that species A is the one which is present at higher concentration in DMF (NEt_4^+) solution while species B is the one which is the major (or even the only) component in the DMSO (K^+) medium. Moreover, the *g* factor difference ($g_A - g_B$), which is 1×10^{-4} in the former solution, is almost three times as large ($g_A - g_B = 2.7 \times 10^{-4}$) in the latter solution. All these observations can be rationalized if we assume that species A corresponds to the *trans* isomer and species B to the *cis* isomer which is stabilized by the presence of K^+ through ion-pair formation.

Table I. Coupling Constants of Single (a_1) and of Two Equivalent (a_2) Protons (Gauss)

Species		DMF (NEt_4^+)	DMSO (K^+)
A	a_1	5.63	6.09
	a_2	1.38	1.43
B	a_1	6.46	7.00
	a_2	1.47	1.50
C	a_H^{CHO}	5.53	6.88
	a_H^{ortho}	1.36	1.50



If our interpretation is correct, then, to the best of our knowledge, this is the first time that different *g* values were measured for two stereoisomers. The large increase of the difference ($g^{trans} - g^{cis}$) in DMSO (K^+) may also be due to the presence of potassium cations which modify the n–π* excitation energies involved in the second-order mixing responsible for the deviation of the *g* factor from the free-electron value.[6] Theoretical calculations on this effect are in progress and will be discussed elsewhere.

Finally we wish to point out that our experiments confirm very nicely the interpretation of the spectra obtained from electrolyzed benzaldehyde solutions as given by Russell and co-workers.[1] We

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[3] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

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[5] C. Corvaja and G. Giacometti, *Ric. Sci. Rend.*, **35**, 1038 (1965).

[6] H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957); see also A. J. Stone, *Mol. Phys.*, **6**, 509 (1963); 7, 311 (1963).

feel, however, on the basis of our results, that the large difference in the coupling constants for the phenylglyoxal semidione radical in DMF solution as compared with DMSO solution is not simply due to a normal solvent effect but to the presence of a large excess of the *trans* form in the first solvent and of the *cis* form in DMSO containing alkali metal ions.

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The Electrochemical Oxidation of Aromatic Hydrocarbons in Methylene Chloride[1]

Sir:

The electrochemical reduction and oxidation of aromatic hydrocarbons in nonaqueous solutions have been reviewed recently.[2] While the electroreductions are characterized by the formation of stable anion radicals, much of the past work[3-6] suggests that the electrochemical oxidations occur by the abstraction of two or more electrons. The successful use of methylene chloride as a solvent in electron spin resonance (esr) studies of hydrocarbon oxidation[7] suggested that electrochemistry in this solvent might provide evidence of the initial formation of cation radicals on electrooxidation. We report here some preliminary cyclic voltammetric and coulometric studies. Recent work by Peover[2,8] and Adams and co-workers[9] has also provided evidence of an initial one-electron abstraction during electrochemical oxidations in acetonitrile and nitrobenzene.

The results of cyclic voltammetric oxidation of 9,10-diphenylanthracene (DPA), rubrene, 1,3,6,8-tetraphenylpyrene (TPP), and tetracene are given in Table I. The general behavior of DPA, rubrene, and TPP was similar and was characterized by independence of anodic peak potential, E_{pa}, with scan rate, v, essentially equal anodic (i_{pa}) and reversal cathodic (i_{pc}) peak currents, an independence of $i_{pa}/v^{1/2}$ with v, and a separation of E_{pa} and E_{pc} of 60–80 mv. These results suggest a reversible one-electron abstraction from the parent hydrocarbon to form a cation radical which is stable during the time necessary for sweep reversal. For tetracene, however, E_{pa} and $i_{pa}/v^{1/2}$ change with scan rate, and cathodic waves on reversal are either absent or very small. Results similar to these are obtained with anthracene. The evidence here indicates a fast chemical reaction following the electron transfer.

Table I. Cyclic Voltammetric Data for the Oxidation of Several Hydrocarbons in Methylene Chloride[a]

Sweep rate, mv/sec	i_{pa}, μa	i_{pc}, μa	$i_{pa}/v^{1/2}$, μa sec$^{1/2}$/v$^{1/2}$	E, *vs.* sce	
				E_{pa}	E_{pc}
9,10-Diphenylanthracene, 1.2 mM					
67	6.2	4.1	24	1.22	1.16
153	8.8	7.8	23	1.22	1.16
222	11.2	11.3	24	1.22	1.16
312	13.7	13.7	24	1.22	1.16
476	16.9	16.8	24	1.22	1.16
714	20.0	21.6	24	1.22	1.16
Rubrene, 0.8 mM					
67	2.6	2.7	9.8	0.81	0.74
153	3.6	3.6	9.1	0.82	0.74
222	4.2	4.5	8.8	0.82	0.74
312	4.9	5.1	8.7	0.82	0.74
476	6.0	6.2	8.7	0.82	0.73
1,3,6,8-Tetraphenylpyrene, 0.5 mM					
67	1.8	1.9	6.8	1.17	1.09
153	2.2	2.5	5.5	1.17	1.09
222	2.6	2.8	5.5	1.17	1.09
312	3.0	3.4	5.4	1.17	1.09
Tetracene, 0.9 mM					
67	10.5	...[b]	40	0.98	..
153	14.7	...[b]	38	1.00	..
222	17.3	...[b]	37	1.01	..
312	19.5	...[b]	35	1.02	..
476	22.9	...[b]	33	1.02	..
714	27.1	...[b]	32	1.02	..

[a] The solution was 0.2 M tetra-*n*-butylammonium perchlorate. The electrode was a platinum disk, 0.031 cm^2 (except for TPP, where the area was 0.021 cm^2). [b] Small cathodic current on reversal.

Unequivocal evidence for a one-electron oxidation was obtained by coulometric oxidations with esr observation of the resulting solutions. For the oxidation of DPA and rubrene 1 faraday per mole of hydrocarbon was consumed when oxidation was carried out at controlled potentials about 0.15 v more positive than E_{pa}. Examination of the oxidized solution by cyclic voltammetry showed a cathodic peak at the same potentials as the cathodic peak obtained on reversal in the unoxidized solution.

The esr spectra of the oxidized solutions, transferred to 3-mm Pyrex tubing without exposure to air, were essentially identical with those obtained by chemical oxidation of the hydrocarbons. The electrogenerated radicals appeared to be stable for days in the sealed tubes at liquid-nitrogen temperature. Tetracene and anthracene when subjected to controlled potential coulometric oxidation showed a current which decayed to steady-state values appreciably higher than the background current; this is further evidence of instability of these cation radicals.

The results suggest that the behavior of the aromatic hydrocarbons depends upon whether or not they are substituted in the positions of high electron density. Cation radicals of substituted hydrocarbons (DPA, rubrene, TPP) are stable, whereas unsubstituted ones (anthracene, tetracene) react rapidly. Adams and coworkers[9] have reached a similar conclusion based on results obtained in nitrobenzene. The cation radicals

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(1) This research was supported by the Robert A. Welch Foundation and the National Science Foundation (GP-1921).

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